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Structural, dielectric and pyroelectrixc properties of La-doped $Pb_5Ge_3O_{11}$ ferroelectric

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Abstract : Polycrystalline samples of lanthanum doped lead germanate were prepared by a solid-state reaction technique Preliminary X-ray studies show that the single phase compound has been formed. Dielectric constant (ε) and loss (tan δ) were measured as a function of temperature (room temperature to 200°C) at two frequencies, 1 kHz and 10 kHz The behaviour of dielectric anomaly and ferroelectric phase transition observed at 162 ± 1°C was supported by our pyroelectric studies. The activation energy of the sample was calculated from the dielectric data.

Keywords : La-doped $Pb_5Ge_3O_{11}$, dielectrics, pyroelectrics

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1. Introduction

Over the last two decades, a lot of work has been done to investigate the physical properties of $Pb_5Ge_3O_{11}$ (PGO) ferroelectric on single crystal, ceramic and thin films for different dielectric and pyroelectric applications [1–8]. It has been found that it is a uniaxial ferroelectric and spontaneous polarization of its single crystal is 4.8 $\mu C/cm^2$ [9]. The unique features of this ferroelectric are, (i) its high quadratic electrooptic coefficient [10] and (ii) its low dielectric constant and relatively high pyroelectric coefficient, hence, a high figure of merit [11]. The value of Curie constant (~10^4) of PGO lies between that of the order-disorder (~10^3) and displacive (~10^5) type of phase transition [12]. At room temperature, it belongs to trigonal crystal class having $P3$ symmetry which transforms to $P\bar{6}$ of hexagonal class of Curie temperature 178°C [13]. It has been found that PGO with the appetite nasonite structure is a good host material for ionic substitution and

hence numerous isomorphous compounds can be formed. Considering the pyroelectric applications, some attempts have to been made to modify PGO with Nd rare-earths ions on thin film samples [14,15]. We have now modified PGO with La^{3+} ion substituting at Pb-site according to the formula $Pb_{5-x}(La_{2/3}\square_{1/3})_xGe_3O_{11}$ (hereafter PLGO). In this paper, we have reported the structural, dielectric and pyroelectric properties of modified lead germanate, PLGO.

2. Experimental details

Polycrystalline samples of the PLGO compound was synthesized by the solid-state reaction technique using high-purity PbO (99.9%, M/s Aldrich Chemical Co., USA), GeO_2 (99.999%, M/s Aldrich Chemical Co., USA), and La_2O_3 (99.8%, M/s Indian Rare Earth Ltd.). Stoichiometric mixture of these oxides was thoroughly mixed in an agate mortar for 3h in wet medium and then dried and calcined at 670°C for 14h in air atmosphere. The cooled material was powdered and the formation of the prepared material was checked by X-ray diffraction technique at room temperature (RT).

From the homogeneous powder of the PLGO, pellet samples (diameter ~6.4 mm and thickness ~1 mm) were prepared by isostatic pressure at 5.5×10^7 kg/m^2 using a hydraulic press. The pellets were sintered at 700°C in air atmosphere for 12h. X-ray diffraction technique was used to check quality and formation of the material. The X-ray diffractogram (XRD) of PLGO was recorded at room temperature in a Philips (PW-1820) X-ray powder diffractometer using CuK_α ($\lambda = 1.5418$ Å) radiation in a wide range of Bragg angle ($15° \leq 2\theta \leq 75°$) at the scanning rate of 2°/min. For the electrical measurements, the sintered pellets were polished with fine emery paper to make both the surfaces flat and parallel. Air drying conducting silver paint was applied to both faces of the samples for better electrical contacts.

Measurements of dielectric constant (ε) and loss (tan δ) of PLGO were carried out using GR 1620 AP capacitance measuring assembly a function of frequency (10^2 Hz to 10^4 Hz) at room temperature and as a function of temperature (27°C to 200°C) at frequencies 1 kHz and 10 kHz in conjunction with a laboratory built three-terminal sample holder. The pyroelectric current was measured with a picoammeter (M/s Scientific Equipment, Roorkee) in the temperature range, room temperature to 200°C at the uniform heating rate of 2°C/min. Before the measurement of pyroelectric current, the poling of the sample was carried out at 100°C in a silicon oil bath using a dc bias field of 10 kV/cm for about 3h.

3. Results and discussion

The sharpness and the single reflection peaks of the XRD pattern of calcined powder (Figure 1) support the formation of single phase compound and the peaks were compared with the XRD pattern of pure lead germanate recorded earlier. The d-values of the peaks were calculated from XRD. The cell parameters of the compound were calculated by using a standard computer program package. These are : $a = 10.229(5)$ Å and $c = 10.670(0)$ Å.

The cell parameters were found very consistent with the reported ones for pure lead germanate [16]. However, some minor shifts in the peak positions have been observed,

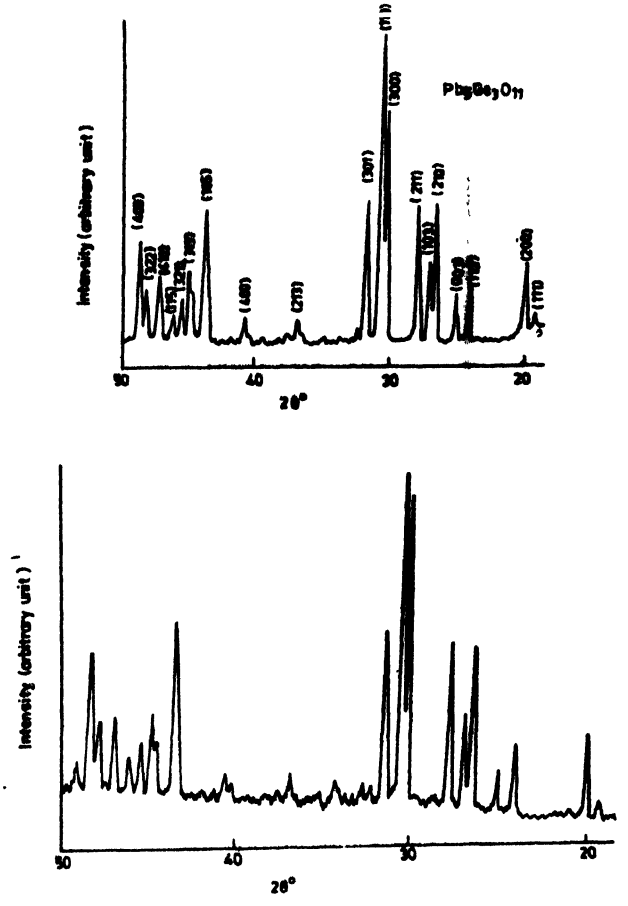

Figure 1. Comparison of XRD pattern of PLGO and PGO.

and hence in *d*-values and cell parameters. The cell parameters are slightly reduced due to the incorporation of small La^{3+} ions in place of Pb ions. Hence, the basic structure of $Pb_5Ge_3O_{11}$ has not been changed on incorporation of La^{3+} ion at the Pb-site. From the diffraction profile of powder diffractogram, coherently scattered domain size of the sample was calculated using Scherrer's equation and found to be 290 Å. The coherently scattered domain size of the sample reported here is of low Bragg angle region, to avoid strain broadening as far as possible. However, instrumental broadening has not been taken into consideration.

The above lattice parameters were used to calculate the theoretical density of the material assuming the number of formula units $z = 3$ per unit cell [17]. The density of PLGO was determined by liquid displacement method and was found to be 6.46 gm/cc which is 87% of the theoretical value. From the comparison of theoretical and measured densities, we found that some pores or voids were present inside the pellet samples.

The variation of dielectric constant (ε) and loss (tan δ) of the compound with frequency (10^2 Hz to 10^4 Hz) at room temperature are shown in Figure 2. It is found that there is no significant change in dielectric constant and loss within the said frequency range

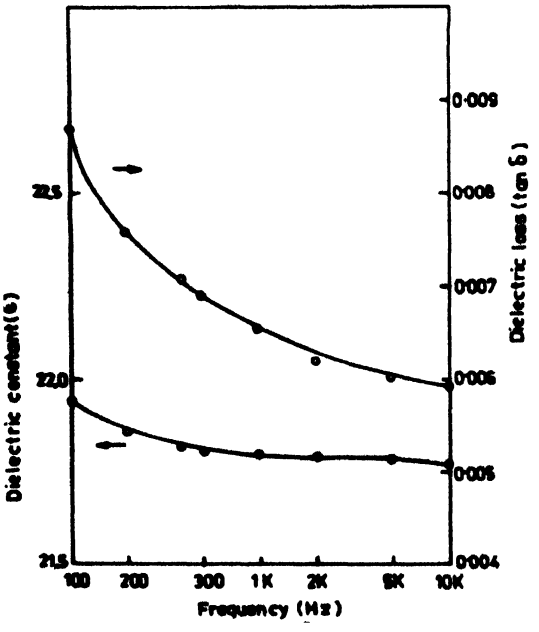

Figure 2. Variation of dielectric constant (ε) and loss (tan δ) of PLGO as a function of frequency at room temperature.

but increases slightly in the lower frequency region. From the study of variation of dielectric constant with frequency, it can be concluded that all the fundamental polarizations are equally active within the measured frequency range.

At 1 kHz and 10 kHz, the variation of dielectric constant and loss of the compound with temperature are shown in Figure 3. It is clear that the material has undergone a phase transition at 162 ± 1°C. The rapid increase in dielectric constant beyond 175°C at 1 kHz is due to the presence of space charge polarization in the compound. The pressed sample develops a considerable amount of space charge polarization arising out from the defects or impurities present in the bulk or at the surface of the material. The contribution of space charge polarization is negligible at high frequencies but noticeable at high temperature. The value of maximum dielectric constant was found to be 50 at 1 kHz and 47 at 10 kHz. The variation of dielectric loss with temperature showed a smooth increasing trend at both frequencies.

As the ionic substitutions create some diffuseness/disordering in the ferroelectric materials, we have calculated the diffusivity γ of the phase transition using the formulae [18]:

$$1/\varepsilon - 1/\varepsilon_{max} = C(T - T_c)^{\gamma},$$

$$\ln\left(1/\varepsilon - 1/\varepsilon_{max}\right) = \ln C + \gamma \ln\,(T - T_c),$$

where ε is the dielectric constant at temperature T, ε_{max} is its maximum value at T_c and C is proportionality constant. The value of diffusivity γ is 1 for a normal ferroelectric that shows

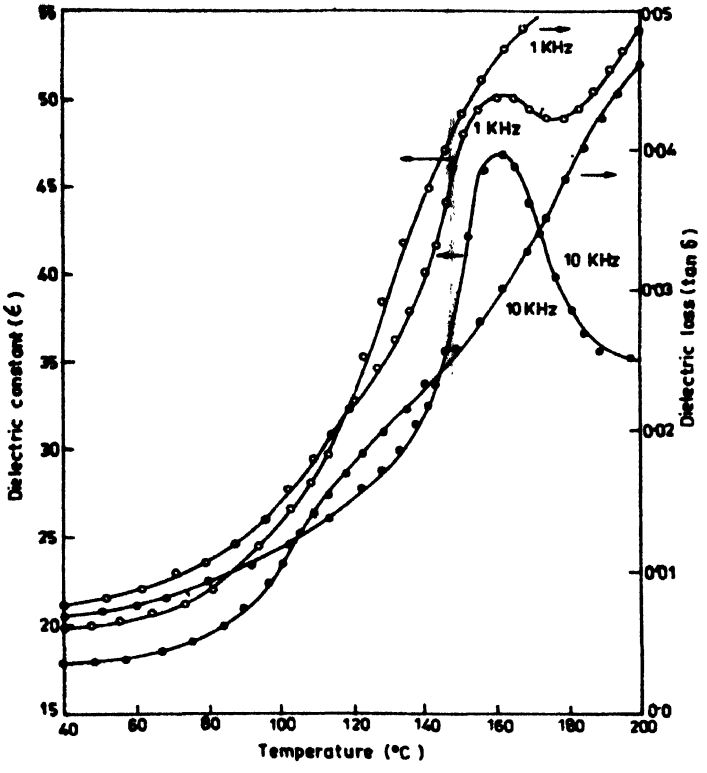

Figure 3. Variation of dielectric constant (ε) and loss (tan δ) of PLGO as a function of temperature at 1 kHz and 10 kHz.

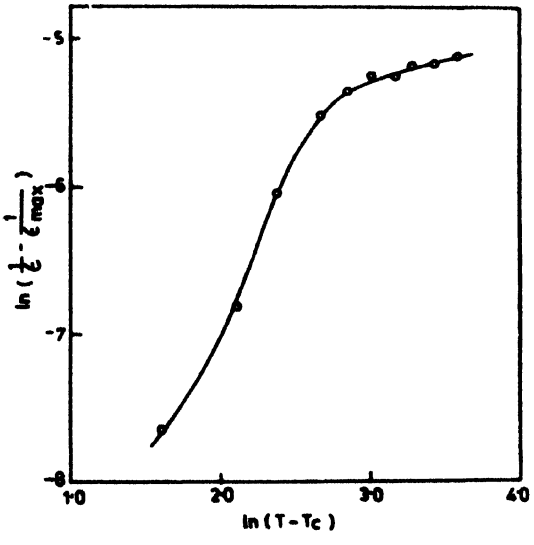

Figure 4. Variation of $\ln(1/\varepsilon - 1/\varepsilon_{max})$ with $\ln(T - T_C)$.

a Curie-Weiss type behaviour and is equal to 2 for diffuse type ferroelectric relaxor. Here, the value of γ calculated from the slope of $\ln(1/\varepsilon - 1/\varepsilon_{max})$ *versus* $\ln(T - T_c)$ (Figure 4) was found to be 1.55 at 10 kHz, which suggests that the material has some diffusive character in its phase transition.

The ac electrical conductivity, σ_{ac}, can be represented by the equation $\sigma_{ac} = \varepsilon\, \varepsilon_0\, \omega \tan \delta$, where ω is the angular frequency and ε_0 is the dielectric constant in free space. Hence the ac conductivity at different temperatures can be determined by simply measuring the dielectric constant and loss at those temperatures. The activation energy is related to σ by the well known relation $\sigma = \sigma_0 \exp[-E_a/K_BT]$. Hence from the slope of the curve of $\ln\sigma_{ac}$ *vs* $1/T$ plot (Figure 5), the value of activation energy (E_a) can be found out. We have calculated the activation energy in the paraelectric high-temperature region, this is because, the effect of extrinsic carrier is much lower than intrinsic carrier in the high-temperature region and found to be 0.47 eV.

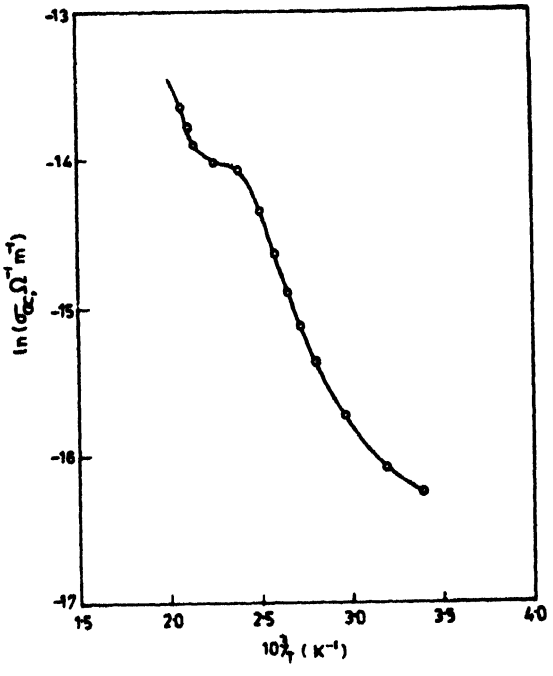

Figure 5. Variation of $\ln\sigma_{ac}$ as a function of inverse absolute temperature $10^3/T$ at 10 kHz.

The variation of pyroelectric coefficient as a function of temperature is shown in the Figure 6. The value of phase transition temperature obtained from pyroelectric measurement for PLGO is in good agreement with the value obtained from dielectric measurement. The maximum value of pyroelectric coefficient at transition temperature was found to be 152 nC/cm^2/K.

Analyzing the above results, we have concluded that the incorporation of La^{3+} ions at Pb-sites lowers the transition temperature of the pure lead germanate, the crystal structure remains same as PGO structure and it can be used as pyroelectric detector material because of its low dielectric constant and loss with relatively high pyroelectric coefficient.

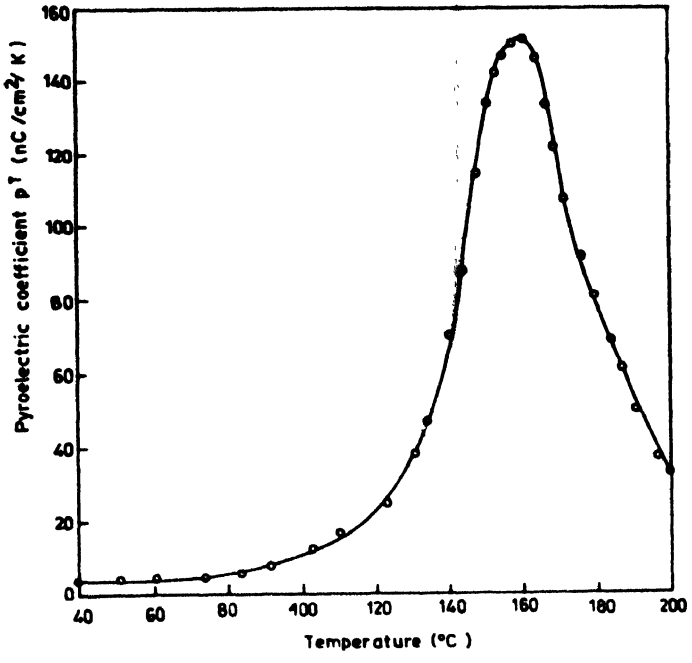

Figure 6. Variation of pyroelectric coefficient as a function of temperature.

However, the actual selection of material may be done only after the measurement of specific heat of the material to determine the figure of merit.

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